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# PATENT SPECIFICATION

1,042,520

NO DRAWINGS.

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Int. Cl.:—C 08 f 15/00 //G 03 c.

## COMPLETE SPECIFICATION.

### Improvements relating to Compositions for Preparation of Photosensitive Films.

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington 98, Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to compositions for preparation of a photosensitive film for use in image reproduction, and to their preparation and use.

Various such compositions suitable for making printing plates and the like are well known. All of these, however, comprise compositions which are applied to a support by coating from an organic solvent system, by extrusion, by hot-pressing or by calendering. All of these techniques have certain disadvantages. For example, the use of organic solvents can be very hazardous and require additional equipment for safe handling as well as a solvent recovery system. Any of the other techniques which involve intensive or prolonged heating of the compositions requires the exercise of care to prevent premature polymerization or other deleterious effects. Further, certain of the known techniques present exceptional difficulties in applying a uniform thickness of the composition onto the support.

The present invention provides compositions that may be coated from an aqueous medium to form a photosensitive film.

The coating compositions of the invention comprise an aqueous dispersion of a water-

insoluble polymer which is capable of coalescing to form a continuous film on drying, a surface active agent, a non-gaseous ethylenically unsaturated compound containing at least two terminal ethylenic groups having a boiling point above 100°C. at normal atmospheric pressure, and capable of forming a high polymer by free-radical initiated, chain-propagating, addition polymerization, and a free-radical generating, addition polymerization initiator activatable by actinic radiation.

In a preferred method of making these compositions the unsaturated compound is employed as an aqueous solution or dispersion which contains about 10 to 60 percent of said compound, the dispersion of water-insoluble polymer contains about 10 to 60 percent of said polymer, and the ratio of the unsaturated compound to the water-insoluble polymer is about 1:9 to 9:1, calculated on a dry (i.e. water-free) basis.

The coating compositions also preferably contain a colorant such as an organic dye or pigment, e.g. carbon black. It is also advantageous to have present a chain-transfer agent, e.g. one or more of the chain-transfer agents disclosed in United States Patent No. 3,046,127, in the amounts given in that patent, especially a polyethylene oxide of a molecular weight of about 500 to about 20,000.

The photopolymerizable compound should be non-volatile and should be soluble or dispersible in water, with the aid if necessary of a surface active agent. In the most useful systems, the photopolymerizable compounds are compatible with or soluble in the dried non-polymerizable polymer contained in the aqueous dispersion, but

images may be obtained from systems in which this compatibility or solubility requirement is not met. Addition polymerizable ethylenically unsaturated compounds suitable for use in the invention include unsaturated esters of polyols, particularly such esters with alpha-methylene carboxylic acids, e.g., ethylene diacrylate, diethylene glycol diacrylate, glycerol diacrylate, glycerol triacrylate, mannitol polyacrylate, sorbitol polyacrylates, ethylene dimethacrylate, 1,3-propanediol dimethacrylate, 1,2,4-butanetriol trimethacrylate, 1,4-cyclohexanediol diacrylate, 1,4-benzenediol dimethacrylate, isosorbidediacrylate, pentaerythritol di-, tri- and tetra-methacrylate, dipentaerythritol polyacrylate, pentaerythritol di-, tri-, and tetraacrylates, 1,3-propanediol diacrylate, 1,5-pentanediol dimethacrylate, the bis-acrylates and methacrylates of polyethylene glycols of molecular weight 200 to 4000; unsaturated amides, particularly those of the alpha-methylene carboxylic acids, and especially those of alpha, omega-diamines and oxygen-interrupted omega-diamines, such as methylene bisacrylamide, methylene bis-methacrylamide, ethylene bis-methacrylamide, 1,6-hexamethylene bis-acrylamide, diethylene triamine tris-methacrylamide, 1,2-di(gamma-methacrylamidopropoxy)ethane, beta-methacrylamidoethyl methacrylate, N-(beta-hydroxyethyl)-2-(methacrylamido) ethyl acrylate and N,N-bis(beta-methacryloxyethyl)acrylamide; vinyl esters such as divinyl succinate, divinyl adipate, divinyl phthalate, divinyl terephthalate, divinyl benzene-1,3-disulfonate, and divinyl butane-1,4-disulfonate, and unsaturated aldehydes, such as sorbaldehyde (hexadienal). An outstanding class of these preferred addition polymerizable components are the esters and amides of alpha-methylene carboxylic acids and substituted carboxylic acids with polyols and polyamines wherein the molecular chain between the hydroxyls and amino groups is solely carbon or oxygen-interrupted carbon. The amount of monomer added varies with the particular thermoplastic polymer used and with the system of development to be used.

The dispersions of polymers useful in this invention include any aqueous dispersions which will coalesce to form a film on drying, preferably a continuous film, optionally with the application of heat. These include most commercially available polymeric dispersions. Useful products of different types may be obtained depending on whether or not the polymer of the dispersion is compatible with the monomer. In the case where they are not compatible, a coating of the polymer dispersion and monomer results in a connected network of polymer which holds the monomer like

a sponge. This occurs, for example, when coating a composition comprising a monomer such as polyethylene glycol diacrylate and a dispersion such as a natural or synthetic rubber latex.

The most useful products of this invention have been those in which the photopolymerizable monomer and the polymer give a compatible mixture after coating and drying, i.e., the monomer and polymer form a single phase in which the monomer serves as a plasticizer for the polymer.

Useful dispersions of water-insoluble polymers and copolymers may be obtained by emulsion polymerization of ethylenically unsaturated monomers and mixtures of such monomers comprising vinyl esters (e.g., vinyl acetate, vinyl benzoate), vinyl ethers (e.g., methyl vinyl ether), vinyl and vinylidene halides (e.g., vinyl chloride, vinylidene chloride, vinyl fluoride), vinyl cyanides (e.g., methacrylonitrile), acrylic and alkacrylic esters (e.g., butyl methacrylate), halogen substituted acrylic esters (e.g., methyl alpha-chloro-acrylate), acrylic acid, butadiene, styrene, 2-chloro-butadiene and vinyl heterocycles (e.g., vinyl pyrrolidone and vinyl pyridine). Mixtures of polymers and copolymers may be used.

In addition, preformed polymers may be dispersed in water under appropriate conditions, e.g., polyethylene, cellulose esters (e.g., cellulose acetate), cellulose ethers (e.g., ethyl cellulose), polyesters, e.g., polydiethylene glycol sebacate, copolyesters (e.g., polyethylene glycol hexahydroterephthalate/terephthalate/sebacate), nylons, polyformaldehyde, polyurethanes, polycarbonates. Ordinarily these dispersions may be prepared by mixing a solution of the polymer in an appropriate solvent with water, usually with vigorous agitation, and with the aid of a surface active agent, optionally followed by removal of the solvent by evaporation, steam distillation, etc. A colloid mill, or other means for providing vigorous agitation, may be used. In general, however, it is preferable to use polymeric dispersions obtained by emulsion polymerization because of their lower cost.

A preferred class of free-radical generating addition polymerization initiators activatable by actinic light and thermally inactive at and below 185°C. includes the substituted or unsubstituted polynuclear quinones which are compounds having two intracyclic carbonyl groups attached to intracyclic carbon atoms in a conjugated carbocyclic ring system. Suitable such initiators include 9,10-anthraquinone, 1-chloro-9,10-anthraquinone, 2-chloro-9,10-anthraquinone, 2-methyl-9,10-anthraquinone, 2-ethyl-9,10-anthraquinone, 2-tert-butyl-9,10-anthraquinone, octamethyl-9,10-anthraquinone, 1,4-naphthoquinone, 9,10-

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phenanthrenequinone, 2- and 3-carboxy-9,10-phenanthrenequinone and their alkali metal or ammonium salts, 1,2-benzanthraquinone, 2,3-benzanthraquinone, 2-methyl-1,4-naphthoquinone, 2,3-dichloro-1,4-naphthoquinone, 1,4-dimethyl-9,10-anthraquinone, 2,3-dimethyl-9,10-anthraquinone, 2-phenyl-9,10-anthraquinone, 2,3-diphenyl-9,10-anthraquinone, sodium salt of 9,10-anthraquinone alpha-sulfonic acid, 3-chloro-2-methyl-9,10-anthraquinone, retene-9,10-quinone, 7,8,9,10-tetrahydronaphthacenequinone, and 1,2,3,4-tetrahydrobenz (a) anthracene-7,12-dione. Other photoinitiators which are also useful, even though some may be thermally active at temperatures as low as 85°C., are described in Patent Specifications Nos. 741,294, 741,441 and 741,470 and include vicinal diketones compounds, such as diacetyl, benzil;  $\alpha$ -ketaldonol alcohols, such as benzoin, pivaloin; acyloin ethers, e.g., benzoin methyl and ethyl ethers;  $\alpha$ -hydrocarbon substituted aromatic acyloins, including  $\alpha$ -methylbenzoin,  $\alpha$ -allylbenzoin, and  $\alpha$ -phenylbenzoin.

The surface active agent may be used in amounts from 0.05% to 10% by weight of the total coating dispersion. However, no more surface active agent is ordinarily used than is required to mix together a compatible coating dispersion. Commercial polymer dispersions ordinarily are held in suspension by a surface active agent. This may be any one of a number of natural or synthetic surface active agents. If the monomer, photoinitiator, dye, etc. are all water soluble or water dispersible, it may not be necessary to add any additional surface active agent. More usually, additional surface active agent is added. A useful technique is the formation of an emulsion from a monomer in which the photoinitiator is dissolved with the aid of a surface active agent, followed by the mixing this emulsion with the dispersion of the polymeric binder. (After standing a short time, the polymer particles become swollen with the monomer-initiator combination).

Surface active agents that may be used include anionic surface active agents, e.g., sodium lauryl sulfate, sodium dioctyl sulfosuccinate, cationic surface active agents, e.g., cetyl pyridinium bromide, alkylphenoxymethyl - dimethylbenzylammonium chloride, nonionic surface active agents, e.g., nonylphenoxypoly(ethyleneoxy)ethanol, polyoxyethylene sorbitan monopalmitate, and amphoteric agents, e.g., the disodium salt of N-alkyl- $\beta$ -iminodipropionate, the sodium salt of 2-alkyl-1-( $\beta$ -hydroxyethyl)-1-(carboxymethyl)imidazolinium hydroxide. The final coating composition may contain several different types of surface active agents. However, combinations of nega-

tively charged agents, e.g., for the polymer dispersion, with positively charged agents, e.g., for emulsification of a monomer, are inoperable.

Suitable thermal polymerization inhibitors can also be used in photopolymerizable compositions and these include p-methoxyphenol, hydroquinone, and alkyl and aryl-substituted hydroquinones and quinones, *tert*-butyl catechol, pyrogallol, copper resinate, naphthylamines, beta-naphthol, cuprous chloride, 2,6-di-*tert*-butyl p-cresol, phenothiazine, pyridine, nitrobenzene and dinitrobenzene. Other useful inhibitors include p-toluquinone and chloranil.

Other useful additives are the sensitometric modifiers disclosed in Patent Specification No. 13867/63 (Serial No. 1,001,834).

Suitable dyes, pigments, thermographic compounds and color-forming components are disclosed in Patent Specification No. 45522/62 (Serial No. 1,008,183). Also disclosed in the aforementioned patents are useful thermal inhibitors, plasticizing compounds, inert fillers, non-thermoplastic compounds (e.g., materials useful in improving adhesion), supports upon which the photopolymerizable composition may be coated, and image-receptive supports to which the images may be transferred. Furthermore, those applications disclose suitable methods of exposure of the photopolymerizable element, including reflectographic methods as well as exposure through transparencies, suitable radiation sources for making the exposures, and appropriate methods for transferring the underexposed image areas to an image-receptive support. In addition, they disclose suitable coating methods or methods of applying the photopolymerizable composition to a support.

The photopolymerizable compositions of this invention can be applied to a wide variety of supports, chosen according to the desired use of the resultant element. Patent Specification No. 905,700 discloses a number of suitable supports, both flexible and rigid, which are used with the thermal transfer elements described in that application. Suitable supports may also be prepared from polyolefins, e.g., polyethylene and polypropylene. The supports can have an anti-blocking or release coating, e.g., finely divided inert particles in a polymeric binder such as silica in gelatin. In addition to elements of this type, the present invention is also concerned with compositions useful in preparing photopolymerizable plates which are normally coated on metal supports. Patent Specification No. 864,041 discloses many supports suitable in elements of the printing plate embodiment of the present invention.

After imagewise exposure, underexposed

monomer and other ingredients soluble in it, e.g., dye, may be removed by mechanical means such as washing out, squeezing out under pressure, etc., whereas exposed polymerized monomer is not removed by these means. Underexposed areas of a photopolymerizable stratum have only moderate cohesive forces, whereas exposed areas have strong cohesive forces under the same conditions.

The coated elements containing the compositions of this invention may be protected against the effects of oxygen inhibition by exposure in a vacuum printing frame, by a removable cover sheet as described in Patent Specification No. 801/62 (Serial No. 1,001,831), or by being overcoated with a cover stratum comprising at least one wax as described in the aforementioned Patent Specification No. 45522/62 (Serial No. 1,008,183). The wax overcoating may be applied from an aqueous dispersion, as a melt, or from an organic solvent system.

An element containing the compositions of this invention may be used in an image-reproducing process including the steps of exposing said element imagewise to actinic radiation at atmospheric conditions until polymerization, with an accompanying increase in "stick" temperature, of the photopolymerizable stratum takes place in the exposed image areas with substantially less polymerization and less increase in "stick" temperature in the underexposed, complementary, adjoining coplanar image areas to provide a difference of at least 10°C in the "stick" temperatures of said exposed and underexposed areas. At this point, if the element contains a removable cover stratum, said cover sheet is removed.

The image corresponding to the underexposed image areas may be thermally transferred by bringing the surface of the exposed element into operative contact with the surface of an image-receptive support and subsequently separating the two surfaces at an operating temperature intermediate between the "stick" temperatures of the exposed and underexposed image areas. When the element contains a cover stratum comprising a wax, the cover stratum is transferred to the image-receptive support along with the image. In this case, the operating temperature must, in addition to meeting the requirements just stated, also be at least equal to the melting point of the wax in the cover stratum. By exposure and transfer operations as described above, at least one copy of an original image can be obtained. Multiple copies can be obtained by repeating the transfer process using appropriate coating thicknesses of the stratum, pressures and

temperatures to give the desired number of copies.

In discussing the invention in relation to thermal transfer, certain definitions are useful. The term "underexposed" as used herein is intended to denote the image areas which are completely unexposed or exposed only to the extent that there is addition polymerizable compound still present in sufficient quantity that the softening temperature remains substantially lower than that of the complementary exposed image areas. The term "stick temperature", as applied to either an underexposed or exposed area of a photopolymerizable stratum, means the temperature at which the image area in question sticks or adheres (transfers), within 5 seconds, under slight pressure, e.g., thumb pressure, to analytical paper (Schleicher & Schull analytical filter paper No. 595) and remains adhered in a layer of at least detectable thickness after separation of the analytical paper from the stratum. The term "operating temperature" means the temperature at which the operation of transferring the image from the photopolymerizable stratum to the image-receptive surface is actually carried out. The operating temperature is intermediate between the "stick" temperatures of the underexposed and exposed areas of a photopolymerizable stratum.

An element employing the compositions of the invention may have other useful applications when, after the exposure step, the element is dusted with a powder, pigment, or phosphor as described in Patent Specification No. 945,807, or when it is contacted with a layer from which a powder or pigment may be stripped as described in the Patent Specification No. 935,627. These dusted or stripped elements may be useful *per se* or may be used as a matrix for subsequent transfer of an image to a receptor support such as bond paper.

Elements of the invention have other important applications as photopolymerizable printing plates which may be manufactured by the improved process of coating from an aqueous medium. Such elements may be used as planographic or letter press printing plates, but preferably the former since thinner coating layers (e.g., about 0.002 inch (0.05 mm) or less in thickness) of the photopolymerizable composition can be used with a planographic type of plate. After exposure to actinic radiation, the plates may be developed in various ways, e.g., by washout of the underexposed image areas such as described in Patent Specifications Nos. 741,294, 741,441 and 741,470 or by dry thermal transfer to a porous matrix in order to remove the underexposed image area in a molten form

as described in Patent Specification No. 25698/63 (Serial No. 1,042,519).

Since the compositions of this invention have rather wide application, the coated elements comprising these compositions may vary considerably in thickness of the coated stratum. Elements useful in the thermal transfer of images may have coated strata as thin as 0.01 mil (0.0025 mm). Printing plates comprising these compositions, on the other hand, may have coated strata up to about 250 mils (0.635 cm) in thickness. Thick layers may be applied as a single sheet or the desired thickness may be achieved by applying multiple coatings. In the case of multiple coatings, the various layers may be substantially identical or there may be variations in the compositions, e.g., in the amounts or types of initiators and/or inhibitors. In Patent Specification No. 867,957 advantages are disclosed in preparing multilayer elements in which the layers differ in their sensitivity to actinic radiation.

The invention will be further illustrated by, but is not intended to be limited to, the following detailed examples wherein the abbreviation CI refers to the *Colour Index*, 2nd Edition 1956.

#### EXAMPLE I

An aqueous copolymeric dispersion was prepared according to a procedure similar to that described in Example I of Patent Specification No. 718,422, by emulsion polymerization of a mixture containing:

Vinylidene chloride	...	...	85.0 g.
Methyl acrylate	...	...	15.0 g.
Itaconic acid	...	...	2.0 g.
Water	...	...	100.0 g.
Ammonium persulfate	...	...	0.50 g.
Sodium metabisulfite	...	...	0.25 g.
Sodium dodecyl sulfate mixture*	...	...	2.00 g.

\*A mixture of sodium alkyl sulfates of 8 to 16 carbon atoms predominating in sodium dodecyl sulfate.

This dispersion was diluted with water to 20% by weight of solids.

Fifty grams of a 20% by weight aqueous solution of polyethylene glycol diacrylate (derived from polyethylene glycol with an average molecular weight of 300) was mixed with 50 grams of the 20% by weight copolymeric dispersion described above and to this was added a solution containing the following:

100 ml.	Water
0.12 g.	Sodium anthraquinone beta-sulfonate
0.10 g.	Dye (CI Direct Violet 9)

The above mixture was coated to a dry thickness of about 0.001 inch on a 0.004 inch thick polyethylene terephthalate film support bearing a subcoat of a copolymer of vinylidene chloride/methyl acrylate/itaconic acid as disclosed in Alles et al., Patent Specification No. 718,422. The dried coating was laminated at room temperature to a sheet of 0.001 inch thick polyethylene terephthalate film by passing the coated support and the superposed cover film together through rollers pressed together with a force of 2 pounds per lineal inch.

The laminated element was exposed, through a halftone positive, to a 400-watt high pressure mercury-arc lamp, General Electric Co., Type H 400-R1, for 45 seconds at a distance of 20 cm. The 0.001 inch-thick laminated cover film was then stripped from the coating.

Transfer of the underexposed image area was made by laying a sheet of bond paper onto the coating and passing the superposed elements through pressure rollers at 125°C. and  $\frac{1}{2}$  pound of force per lineal inch of the rollers. The paper was separated from the film as it emerged from the rollers. A clear, sharp, positive, violet-colored copy of the original image was thus obtained.

A similar print was made by thermal transfer to a paper lithographic plate. The transferred image was dusted with powdered graphite. This resulted in adhesion of graphite to only the transferred polymer to give a black image. The plate was mounted in a lithographic offset press and a number of copies were printed.

#### EXAMPLE II

Example I was essentially repeated except that the fifty grams of a 20% aqueous dispersion of the copolymer described in that example was replaced with the same amount of 20% aqueous dispersions of various other polymers as listed below:

- A. A butadiene/acrylonitrile copolymer rubber dispersion prepared from a mixture of monomers containing about 60% by weight butadiene and about 40% by weight acrylonitrile, dispersed with soap, according to the procedure given in Whitby, *Synthetic Rubber*, p. 802 (1954) John Wiley & Sons, New York. The size of the dispersed particles was about 180 m $\mu$ .
- B. A polyvinyl acetate dispersion was prepared by the general procedure for emulsion polymerization of vinyl acetate given in Sorenson and Campbell, *Preparative Methods of Polymer Chemistry*, p. 173 (1961), Interscience Publisher, New York, using about 4.5 grams of polyvinyl alcohol per 100 grams of monomers as emul-

- sifying agent. Polymer isolated from the dispersion was found to have a molecular weight of about 50,000.
- C. A copolymer prepared by emulsion copolymerization of 98 parts of butyl methacrylate and 2 parts of itaconic acid, using the sodium dodecyl sulfate mixture of Example I as the dispersing agent in the amount of 4.0 g. per 100 g. of monomers.
- D. A dispersion of a copolymer prepared from a mixture containing twenty parts of acrylonitrile and eighty parts of vinylidene chloride in which were also dispersed fifteen parts of a dibutyl phthalate plasticizer per one hundred parts of polymer, using the sodium dodecyl sulfate mixture of Example I as the dispersing agent.
- E. A polyethyl acrylate dispersion prepared by emulsion polymerization of ethyl acrylate, using 4.2 grams of the sodium dodecyl sulfate mixture of Example I per 100 grams of monomer as an emulsifying agent during polymerization.
- F. A commercial dispersion of a copolymer of acrylic acid dispersed with an anionic dispersing agent, sold as a dispersion of 40% by weight solids, with a pH of 3.0, viscosity of 20 cps, and specific gravity of 1.08. The equivalent weight of the dried copolymer was 266, corresponding to an acrylic acid content of 27% by weight, the remainder being an acrylic ester.
- The compositions containing these various aqueous polymeric dispersions were coated and dried, laminated, exposed, delaminated and imagewise transferred to sheets of bond paper, all as described in Example I, to give positive copies of the original image.

#### EXAMPLE III

Twenty ml. of a 20% by weight aqueous dispersion of a synthetic rubber latex containing 54 parts of butadiene and 46 parts of styrene, emulsified with a rosin soap and prepared according to GRS formula No. 2001, was mixed with 20 ml. of a 20% by weight solution of polyethylene glycol diacrylate prepared by mixing the following:

- 400 ml. Water  
1.2 g. Sodium anthraquinone beta-sulfonate  
1.0 g. Dye (CI Direct Violet 9)  
100 g. Polyethylene glycol diacrylate (as described in Example I)

The pH of the mixture, originally 10.2, was adjusted to 7.95 with 0.1 N hydro-

chloric acid. The mixture was then coated to a wet thickness of 0.003 inch on a polyethylene terephthalate drafting film as described in Example X of Van Stappen, Patent Specification No. 871,305. The dried coating was laminated with 0.001 inch thick polyethylene terephthalate film and then exposed through a photographic negative in a vacuum frame exposure unit (Fairchild Exposure Unit Model F3861) with 16 passes of the mercury arc at a distance 1½ inches at a rate of 75 inches per minute. The exposure was determined as being 0.58 watt seconds per square inch per pass. The 0.001 inch-thick cover film was stripped off after exposure and the coating was washed with water so that, by removal of dye but not of the polymer from the underexposed areas, there resulted a dark lavender image against a light lavender background.

#### EXAMPLE IV

A coating mixture was prepared as described in Example III except that the dispersion of the butadiene/styrene copolymer was replaced with a 20% by weight dispersion of the polyethyl acrylate similar to that described in Example II.

The pH of this mixture was 4.05 and was not further adjusted. The mixture was coated, dried, laminated, and exposed as described in Example III except that exposure was reduced to only 4 passes of the mercury arc. After delamination of the cover film, the exposed coating was swabbed with paper tissues alternately soaked in water and alcohol. By differential wet adhesion to the base, the underexposed areas of the polymerizable coating stratum were removed, leaving a dark lavender image in the exposed areas.

#### EXAMPLE V

Coating mixtures were prepared as described in Example III except that the dye was omitted and the dispersion of butadiene/styrene copolymer was replaced with a similar 20% by weight aqueous dispersion of:

- (a) polyethyl acrylate (as described in Example II),  
(b) polybutyl acrylate prepared by emulsion polymerization of butyl acrylate in the presence of 1.5 g. of disodium N-alkyl-β-iminodipropionate per 100 grams of monomer, in which the alkyl substituent of the surface active agent consisted of a mixture of straight chain aliphatic radicals of fourteen to eighteen carbon atoms,  
(c) poly-2-ethylhexyl acrylate prepared by emulsion polymerization of 2-ethylhexyl acrylate in the presence



of 1.5 g. of disodium N-alkyl- $\beta$ -imino-dipropionate per 100 grams of monomer, in which the alkyl substituent of the surface active agent consisted of a mixture of straight chain aliphatic radicals of fourteen to eighteen carbon atoms.

The three coating mixtures were skim coated on separate, short lengths of film base as described in Example IV of Alles, Patent Specification No. 786,176. The coatings were laminated, exposed to 8 passes of the mercury arc and delaminated as described in Example III.

The exposed coatings were swabbed with wet tissues as in Example IV, the tissues being wet merely with water for compositions (b) and (c), while for coating composition (a) the tissues were wet with a solution consisting of one part by weight of acetone to three parts by weight of water. As in Example IV, by differential wet adhesion to the support, the underexposed areas of the polymerizable coating stratum of the three elements were removed, leaving thin relief images of the exposed areas. The relief images were visible, although there was no dye present as in the preceding example. The three coatings were dampened with a 3% by weight colloidal solution of silica (average particle size about 17m $\mu$ ) in order to increase the hydrophilicity of the background areas, then contacted with a commercially available magenta-colored lithographic ink which was diluted with raw linseed oil in order to facilitate manual ink application. This greasy, hydrophobic ink adhered preferentially to the relief image areas (exposed areas) so that the elements could be used as lithographic plates. A number of magenta copies were printed on bond paper by successive applications of 3% colloidal silica and ink, followed by contacting with separate sheets of paper.

#### EXAMPLE VI

A copolymeric dispersion was prepared by reacting 180 g. of vinylidene chloride, 20 g. methyl acrylate, 0.84 g. potassium persulfate and 0.70 g. sodium metabisulfite catalyst and 9.6 g. of the sodium dodecyl sulfate mixture of Example I in sufficient water to bring the total reaction mixture to a weight of 800 g. The reaction mixture was heated at 35–40°C. for about one hour. A coagulated sample of polymer had an inherent viscosity at a concentration of 0.5% by weight in dimethylformamide of 0.55.

Forty ml. of the resultant 25% by weight aqueous dispersion of the (90/10) vinylidene chloride/methyl acrylate copolymer was mixed by stirring with 20 ml. of a

4% by weight dispersion of colloidal carbon (average particle diameter 9 m $\mu$ ) which had been sand milled to substantially eliminate any aggregation of the particles. Twenty ml. of distilled water was added and the pH adjusted to 6.5 with dilute sodium hydroxide solution. To 10 g. of triethyleneglycol diacrylate there was added 0.1 g. of 2-ethylanthraquinone and the mixture was dispersed by stirring into 30 ml. of a 3% by weight aqueous solution of *p*-(1,1,3,3-tetramethylbutyl) phenoxy polyethylene glycol containing about 40 ethylene oxide units per molecule. This dispersion was mixed by stirring with the above copolymer dispersion containing the colloidal carbon.

The mixture was coated on 0.004-inch thick polyethylene terephthalate film base to give a dry coating thickness of film about 0.0003 inches. The coating was laminated with 0.001-inch polyethylene terephthalate film and exposed through a negative to 8 passes of the mercury arc in a vacuum frame exposure unit as described in Example III but employing a  $\frac{1}{4}$ -inch deep honeycomb screen over the lamp to partially collimate the light. This technique gave exposure of about 0.20 watt seconds per square inch per pass. The laminating cover sheet was removed, and transfer of the underexposed image area was made to bond paper as described in Example I, giving an excellent black copy of the original image against a white background. Similarly, transfer was made to a drafting film surface as described in Example 10 of Patent Specification No. 871,305, giving a good copy of the original image.

The above experiment was essentially repeated except that the 20 ml. of colloidal carbon dispersion in the coating mixture was replaced with a like volume of a 5% by weight aqueous solution of Acid Magenta O dye (CI Acid Violet 19). In this case, clear magenta images were obtained upon transfer both to paper and to drafting film.

#### EXAMPLE VII

A 25% dispersion of polymethyl methacrylate was made by emulsion copolymerization of 200 g. of inhibitor-free methyl methacrylate in 574 g. of water containing 14.4 g. of the sodium dodecyl sulfate mixture of Example I, 9.8 ml. of 18% hydrogen peroxide polymerization catalyst and 225 g. of carbon tetrachloride chain transfer agent. The polymerization was conducted for forty-two minutes at about 75°C., after which the carbon tetrachloride was removed by steam distillation, and the final weight was adjusted to 800 g. by addition of water. A portion of the dispersion was treated with acetone to precipitate the polymer which was dried and found to have an in-



herent viscosity of 0.36, determined at 0.5% by weight concentration in acetone. A second dispersion was prepared by this same procedure, except that 200 g. of butyl methacrylate was substituted for the 200 g. of methyl methacrylate. A coagulated and dried sample of the latter polymer was found to have an inherent viscosity of 0.53. A mixture was made of 12.0 ml. of the polymethyl methacrylate dispersion with 28.0 ml. of the polybutyl methacrylate dispersion, the pH of the mixture was adjusted to 6.5 with dilute aqueous sodium hydroxide solution, and 20 ml. of water was added. A mixture of 10 ml. of a 1% solution of 2-ethyl-9,10-anthraquinone in polyethyleneglycol diacrylate as described in Example I and 10 ml. of a 2% by weight aqueous solution of the sodium dodecyl sulfate mixture of Example I was made up to give a clear solution. If this solution were stored for more than about an hour, crystals of the insoluble 2-ethyl-9,10-anthraquinone would separate. Therefore, the solution was mixed in a relatively short time with the mixed copolymer dispersion described above. After being mixed with the dispersion, the 2-ethyl anthraquinone did not separate, indicating that it was dissolved in the dispersion particles. To this solution was added 2 ml. of a 3% solution of cetyl betaine (coating aid) and 5 ml. of a 5% by weight aqueous solution of Calcocid green (CI Acid Green 50).

The composition was coated at about 0.001 inch-dry-thickness by skim coating on subcoated polyethylene terephthalate film base as described in Example I and then dried.

Exposure was made through a negative with eight passes on the mercury arc, using a honeycomb screen as described in Example VI. Transfer of underexposed material was made to paper at 125°C. resulting in a positive image on the paper.

#### EXAMPLE VIII

A 25% copolymeric dispersion was prepared as in Example VII, substituting 100 g. of methyl acrylate and 100 g. of butyl acrylate for the single monomer of that example, and substituting 1.0 g. of lauryl mercaptan for the 225 g. of carbon tetrachloride, and reducing the sodium dodecyl sulfate mixture from 14.4 g. to 9.6 g. The inherent viscosity of a coagulated, dried sample of the polymer formed was found to be 0.27 measured at 0.5% by weight in acetone. A coating composition was made up as described in that Example, except that 40 ml. of the copolymeric dispersion was substituted for the mixture of homopolymeric dispersions. This material was

skim coated on the polyethylene terephthalate film base described in Example I and dried to give a coating of thickness about 0.001 inch, and the coating was laminated as described in Example I.

Exposure of a sample through a negative to radiation from a carbon arc for about one second, followed by delamination and transfer under pressure at temperatures from 50°C. to 125°C. to bond paper gave good positive images on the paper, or on the matte surface of a drafting film as described in Example V of Van Stappen, Patent Specification No. 871,305. A similar coating was made except that the dye was omitted. Exposure was made through a negative using either one or two passes of the Fairchild exposure unit, using a honeycomb screen to collimate the light and reduce its intensity as described in Example VI. After delamination and thermal transfer to bond paper at 100°C., both the bond paper and the exposed coating used for transfer were dusted with iron powder obtained by reduction of iron carbonyl (particle diameter was 3 to 10 microns). This resulted in a positive image on the paper and a negative image on the coating.

#### EXAMPLE IX

To 13 grams of a 34% by weight polyvinyl acetate dispersion comprising 0.065 grams of sodium dodecyl benzene-sulfonate and 0.055 grams of *p*-(1,1,3,3-tetramethylbutyl) phenoxypolyethylene glycol (as surface active agents), and 0.004 g. of Calcocid Green (CI Acid Green 50) there was slowly added with good stirring, 0.73 g. of a 0.1% by weight solution of 9,10-phenanthrenequinone in polyethylene glycol diacrylate (prepared from a polyethylene glycol of molecular weight about 300). A precipitated dried sample of the polyvinyl acetate had an intrinsic viscosity of about 0.55. The solution was coated on oriented, 0.0015-inch thick polyethylene terephthalate film at 0.005-inch wet thickness, dried for two days in the dark and laminated. The coating was exposed through a negative to six passes of the exposure device described in Example III (3.5 watt seconds per square inch) and a positive image was formed by transfer to bond paper at about 80°C.

#### EXAMPLE X

To 75.0 g. of a 20% solids dispersion of poly(alkyl acrylate co acrylic acid), dispersion F of Example II, was added a solution of 4.9 g. of acrylamide, 0.10 g. of methylene-bis-acrylamide, 0.400 g. of a plasticizer, polyethylene glycol of molecular weight of 4000, and 0.05 g. of Calcocid Green S d (CI Acid Green 50). To 10 ml. of a 5% b

weight solution of the mixed sodium alkyl sulfate salts described in Example I was added with stirring, 2.0 ml. of a solution of 1.0 g. of benzoin methyl ether in 10 ml. of methanol to give a slightly turbid dispersion. This dispersion was added with stirring to the first dispersion containing the polymer, monomer, dye, etc. The mixture was skim coated manually on .004-inch (0.10 mm) biaxially oriented polyethylene terephthalate film which had been treated for adhesion (as described in Example III of Patent Specification No. 25698/63 (Serial No. 1,042,519) and allowed to dry to give a clear, pale green coating. This was exposed through a negative as in Example III, using 16 passes of the exposure device. After exposure, the image could be seen by wetting the film with water. The underexposed areas became white and hazy while the exposed areas remained clear.

An exposed sample was soaked in acetone for four minutes, and washed with tap water which removed underexposed areas and left a pale green positive image. This image was made darker by soaking for one minute in a solution prepared from 100 ml. of water and 0.5 g. of Crystal Violet dye (CI Basic Violet 3), followed by washing under the tap to give a purple positive image on a transparent background.

Alternatively, an exposed sample was swabbed with a tissue wet with a solution made from 50 ml. of a 5% by weight sodium chloride solution and 2 ml. of a 4% by weight sodium hydroxide solution and rinsed under the tap. The swabbing with the solution and rinsing with tap water were repeated two more times to give a positive image in shallow relief on the film. The image was made more visible by dyeing, as before. In another experiment, the exposed sample was soaked in a 0.02% by weight sodium hydroxide solution for two minutes, washed with water, soaked in dye solution for a few seconds, then washed with water and wiped free of excess dye to give a negative image. The dilute alkali swelled the underexposed areas so that they were readily dyed. The exposed areas did not absorb the dye.

The elements of the present invention are useful for a variety of copying, printing, decorative and manufacturing applications. Pigments, e.g.,  $\text{TiO}_2$ , colloidal carbon, metal powders, phosphors, etc., and dyes which do not appreciably absorb light at the wave length being used for exposure or inhibit polymerization can be incorporated in the light-sensitive photopolymerizable layer, and, by use of the instant process, images can be transferred to a receptor support. Multicopies of the images of this process can be obtained from the transferred image. The number of copies pre-

pared is dependent on the photopolymerizable composition thickness as well as the process conditions. The process is also useful for preparing multicolor reproductions. Colorless constituents which form colored compounds when heat is applied or brought into contact with other color forming components are useful in the present transfer process.

Lithographic surfaces can be produced by thermally transferring a hydrophobic layer to a hydrophilic receptor surface or vice versa. The images on the lithographic surface can be made impervious to chemical or solvent attack by post-exposing the lithographic surface. Alternatively a hydrophobic photopolymerizable material may be coated over a hydrophilic surface, and the composite structure exposed imagewise and developed by washout techniques or thermal transfer of the underexposed hydrophobic material.

The transferred images are not only useful for making copies of the original image transparency by dry methods as indicated above, but after transfer of the underexposed areas to a receptor support, the thermoplastic surface can be treated with, e.g., aqueous solutions, dyes, inks, etc., to form colored images. Colored copies of the original image can be obtained when the wet surface is brought into intimate contact with a receptor support and the surfaces separated. Solvents which are used for spirit copying, e.g., ethanol, water, should meter out the dye used and be a non-solvent for the polymer, i.e., the solubility of the dye and binder are important factors in selecting the solvent. The process is also useful because it permits the rapid examination of the printing quality, e.g., of separation negatives and positives, under conditions simulating true printing.

After exposure, the exposed photopolymerized stratum can be brought into intimate contact with a separate support, e.g., a roll of carbon or graphite; a roll coated with pigment dispersions; a roll which has a continuously replenished pigment with or without dyes, thermographic compounds, color forming compounds, hydrophilic and hydrophobic surfaces or a metallized film. Upon heating one or both surfaces to the operating temperature, the areas corresponding to the underexposed areas of the photopolymerized composition are receptive to the material on said roll. A duplicate copy and a reverse copy are formed simultaneously. Multicopies of the image can be made by bringing into intimate contact the image-carrying surface and an image-receptive surface and applying the required amount of heat. The stripping procedure followed by thermal transfer is useful in the preparation of silk screens.